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Title:

Heterogeneity in cellulose pyrolysis indicated from the pyrolysis in sulfolane

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Abstract

In sulfolane (tetramethylene sulfone), which is a good solvent for the primary product, levoglucosan, cellulose is pyrolyzed completely into soluble products without forming any char. Residues during pyrolysis in sulfolane at 200, 240 and 330°C were obtained always as colorless non-carbonized substances. From the change in the crystallinity and crystallite size as compared with the ordinary pyrolysis, a heterogeneous mechanism is indicated for cellulose pyrolysis, starting from a molecule which is less stabilized due to lack of some intermolecular interactions.

Keywords: cellulose, pyrolysis, mechanism, heterogeneous, crystalline, non-crystalline, sulfolane

1. Introduction

Crystalline regions are indicated to be much more stable than the amorphous regions in cellulose pyrolysis. Decrystallized cellulose prepared by ammonia treatment [1] or ball-milling [2] is reported to have a much greater rate in the initial weight loss behavior than the original cellulose. Basch and Lewin [3] compared the weight loss behaviors of various kinds of cellulose samples with different crystallinity under vacuum conditions at 251 ºC and reported that the initial rapid weight loss positively related to the percentage of the less ordered regions (%LOR = 100% - %crystallinity). They also estimated the apparent activation energies in the weight loss behavior of the crystalline and non-crystalline regions as 61.2 and 29.6 kcal/mol, respectively. Similar stabilization of the crystalline region of cellulose is also indicated by other researchers [4-6].

Crystallinity also affects the product composition from cellulose. Cellulose with lower crystallinity forms more char and less volatile products including levoglucosan [6-8]. Golova et al. [7] studied the levoglucosan formation from various kinds of cellulose samples compared with glucose and they reported that levoglucosan yield increases with the increasing crystallinity of cellulose. Thus, pyrolysis mechanisms of the crystalline and non-crystalline regions are very important in understanding the

cellulose pyrolysis.

From the mechanistic viewpoint, Halpern and Patai [9] and Weinstein and Broido [1] proposed the unzipping mechanism of cellulose proceeding along the chains which continue through both ordered and disordered regions from the experimental fact that cellulose crystallinity remains constant up to the 60% weight loss of cellulose. Weinstein and Broido [1] also proposed that this transformation is followed by the initial break down of the polymer into about DP 200. Initial rapid depolymerization is originally reported by Golova et al. [10] followed by several authors [9,11,12]. Paucault and Sauret [12] and Broido et al. [11] speculated that this initial depolymerization occurs at the boundaries between the crystalline and amorphous regions. Kim et al. [13] reported the change in the crystallite size from the *in situ* X-ray diffraction measurement of a tension wood of *Populus maximowiczii* at 320 ºC. They concluded that pyrolytic decomposition of cellulose crystallite is heterogeneous from the results that change in the crystallite size is very small although relative intensity of the crystal reflection decreased and finally disappeared with increasing the heating time. However, pyrolysis mechanisms of the crystalline and non-crystalline regions are still ambiguous because these proposals were made from the analysis of the complex substances including carbonized portions.

Kawamoto et al. [14] reported that cellulose suspended in sulfolane (tetramethylene sulfolane), a good solvent for levoglucosan (the primary product of pure cellulose pyrolysis), is pyrolyzed into the soluble products without leaving any carbonized portions in the residues. This system is suitable for investigating the pyrolysis behaviors of the crystalline and non-crystalline regions in cellulose because no carbonized portions accumulate in the residues. In this paper, the results of the characterization of the residues recovered from the pyrolysis of cellulose in sulfolane by X-ray diffraction method are described, and the pyrolysis mechanisms of the crystalline and non-crystalline regions in cellulose are discussed.

2. Experimental

Cellulose sample (cotton, 100-200 mesh, Toyo Roshi Co.) (10 mg) was suspended in sulfolane (0.5ml) (m.p. 27 °C, b.p. 285 °C, Nacalai Tesque Co.) in an sealed ampoule containing air and heated in a salt bath ($KNO_3/NaNO_3$ = 1/1, w/w) preheated at 200, 240 or 330 °C. After an adequate pyrolysis time, the ampoule was immediately cooled by air-flow for 30 s and subsequently in cold water for 3 min. The reaction mixture was separated into sulfolane-soluble and insoluble portions by filtration. The insoluble portion was washed with sulfolane (2.0 ml) twice and methanol (2.0 ml) twice and dried

in an oven at 105 °C for overnight. Pyrolysis in dioctyl phthalate (m.p -50 °C, b.p. 384 °C, Nacalai Tesque Co.) was also conducted in a similar way. Pyrolysis of cellulose (10 mg) in nitrogen was carried out in a flask (30 ml) made of glass attached with nitrogen bag through three-way tap after replacing the air in the reaction system with nitrogen.

Characterization of the soluble portion and IR analysis of the insoluble portion were already reported in the previous paper [14]. X-ray diffraction diagrams of the colorless residues obtained from the pyrolysis in sulfolane and brown to black colored substances obtained from the pyrolysis in nitrogen or dioctyl phthalate were recorded with a Rigaku RINT 2000V (Cu-Kα, λ = 1.542 Å, 40kV, 30mA).

Crystallinity was estimated according to the equation (1) reported by Segal et al. [15]:

$$CrI = [(I_{002} - I_{am}) / I_{002}] \times 100 \qquad (1)$$

where CrI expresses the relative degree of crystallinity, I_{002} is the maximum intensity of the 002 lattice diffraction at $2\theta = 22.8^{o}$ and I_{am} is the intensity of diffraction at $2\theta = 18^{o}$. Crystallite size is estimated according to the Scherrer equation (2) [16] using the

002 lattice diffraction at $2\theta = 22.8^{o}$:

$$L = 0.9\,\lambda / (H \cos\theta) \qquad (2)$$

where L is the crystallite size perpendicular to the plane, λ is the X-ray wavelength, H is the full width at half maximum, and θ is the Bragg angle.

3. Results

Kawamoto et al. [14] describes that cellulose was pyrolyzed in sulfolane into completely soluble products at 330, 240, and 200 °C for 3, 60 and 480 min, respectively, with the main low molecular-weight products including levoglucosan, levoglucosenone, furfural and 5-hydroxymethyl furfural (5-HMF). The residues obtained in the course of the transformation are also described as colorless substances without any formation of the carbonized portions as indicated by their color and IR spectra, which are very similar to that of the original cellulose. From these results, a pyrolysis mechanism starting from the “surface molecule” like “peeling reaction” is proposed [14]. In this mechanism, levoglucosan, the primary pyrolysis product of pure cellulose, formed from

the “surface molecule” is solubilized into the solvent, and this inhibits the ring-opening polymerization of levoglucosan, which is proposed as a key reaction for carbonized product formation [17].

Figure 1 shows the X-ray diffraction profiles of the residual cellulose obtained in sulfolane at 330 ºC for 1 and 2 min, compared with that of the original cellulose. Although the recovery (undissolved residue) decreases into 41 and 19.5%, respectively, detectable change is not observed in their X-ray diffraction profiles. Similar trends were observed also for the residual cellulose obtained at 240 and 200 ºC.

Change in the crystallinity and crystallite size estimated from the X-ray diffraction profile is summarized in Fig. 2 as a function of the pyrolysis time, together with the recovered yield of the residual cellulose. Crystallite size along the chain direction is shown as a relative value against the original cellulose. At all temperatures, yield of the residual cellulose decreases with increasing the pyrolysis time, while both crystallinity and relative crystallite size do not change so much. Furthermore, crystallinity and relative crystallite size are well correlated with the amount of the residual cellulose, respectively, as shown in Fig. 3, although reactivity is different depending on the temperature. This indicates the similar mechanism involved in the pyrolysis in these temperature ranges.

In nitrogen or dioctyl phthalate, a poor solvent for levoglucosan, cellulose was pyrolyzed into the carbonized substances at 330 °C. From the X-ray analysis, relative intensity of the crystal reflection of the 002 lattice diffraction (2θ = 22.8°) decreased with the pyrolysis time and completely disappeared at 15 min as shown in Fig. 4a. On the other hand, change in the relative crystallite size is comparatively small (Fig. 4b) in agreement with the results reported by Kim et al. [13]. Similar relationships are observed under these two pyrolysis mediums.

4. Discussion

Interaction of cellulose and solvent has been extensively studied. Aprotic polar solvents such as dimethylsulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF) are known to swell cellulose, and this property is reported in relation to the loss of the mechanical strength of paper [18]. Arslanov [19] reported that DMSO treatment leads to intercrystallite swelling of cellulose and does not penetrate the crystalline region. From this information, sulfolane, a similar aprotic polar solvent, is expected to penetrate the non-crystalline region of cellulose and remove the initial pyrolysis products including levoglucosan from the pyrolysis site through their solubilization. If sulfolane can penetrate the noncrystalline region completely, crystallinity is expected to

increase through selective removal of the non-crystalline regions of the molecule, in analog to the microcrystalline cellulose preparation by acid hydrolysis [20]. However, as shown in Fig. 2, crystallinity remains rather constant during pyrolysis in sulfolane. These considerations indicate that some of the non-crystalline region persist in contact with sulfolane.

It is also noted that carbonization does not proceed even in the non-crystalline region of the residual cellulose in sulfolane. This was also confirmed by the IR spectrum of the residual cellulose; absorption at 1700 cm^{-1}, assigned to the carbonyl moiety, was completely absent [14], although this signal was observed significantly in the spectra of the carbonized cellulose obtained from the pyrolysis in nitrogen or dioctyl phthalate. Because heat is considered to be supplied to the cellulose molecule during the pyrolysis in sulfolane, these results strongly indicate that the cellulose molecule which can not associate with sulfolane is stable even in its non-crystalline regions at 330 ^{o}C. A rather constant crystallite size observed in sulfolane also supports this hypothesis. If each crystallite is pyrolyzed from the boundary region between crystalline and non-crystalline regions, as like the proposed unzipping mechanism proceeding along the cellulose chains through the active group formed by the initial rapid DP reduction step [1], the crystallite size should decrease with the progress of the

pyrolysis.

These observations are rationally explained by introducing a heterogeneous mechanism for cellulose pyrolysis in sulfolane as illustrated in a simplified model shown in Fig. 5. Pyrolysis reactivity of the cellulose molecule in non-crystalline region is different depending on the extent of the packing. There are two types (A and B) of cellulose molecules that exist in the non-crystalline region depending on the accessibility of sulfolane; type A can associate with sulfolane, while type B can not. The type B molecule which is intimately associated with the surrounding other molecules is considered to be stable even in the non-crystalline region through intermolecular interactions such as hydrogen bonding and hydrophobic interaction. On the other hand, the type A molecule in the disordered region where sulfolane can penetrate is considered to be much less stable due to lack of this stabilization effect at least from one side of the molecule. Consequently, pyrolysis is considered to start from the type A molecule and proceed into the inner part. In this mechanism, a crystallite decomposes in a heterogeneous manor.

Similar behavior of the change in the crystallite size is observed in nitrogen and dioctyl phthalate (Fig.4), and this suggests that a similar heterogeneous mechanism is also operating in a typical pyrolysis that forms carbonized substances. Pyrolysis is

considered to start also from the less stabilized molecule like type A molecule for the pyrolysis in sulfolane, while some of the initial products are converted to the carbonized substances without sulfolane.

From the comparison of Figs. 2a with 4a, pyrolysis in sulfolane proceeds about five times faster than the pyrolysis in nitrogen or dioctyl phthalate. This indicates the acceleration of the pyrolysis reaction of the type A molecule by sulfolane. The reason is not clear at this stage, but the followings are considered. In sulfolane, carbonized substances do not accumulate on the cellulose molecule and this may enhance the pyrolysis reactions. Aprotic polar solvent is known to enhance the ionic reaction, especially the reaction type: A-B $\rightarrow$ $A^+ + B^-$, by stabilizing the transition state, and this characteristic feature is often used in organic synthesis [21]. Pyrolytic mechanism (ionic vs. homolytic) of the glycosidic bond cleavage as a primary pyrolysis reaction of cellulose is still controversial [22], but in ionic mechanism, aprotic polar solvent enhances this pyrolytic reaction trough stabilizing the transition state in the oxonium ion intermediate formation.

4. Conclusions

A heterogeneous mechanism is indicated for cellulose pyrolysis, starting from the

molecule which is less stabilized due to lack of some intermolecular interactions. Cellulose pyrolysis in sulfolane is a very effective way to control the pyrolysis reaction because the molecule which can not associate with sulfolane is stable even in the non-crystalline region.

Acknowledgement

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References

[1] M. Weinstein, A. Broido, Combust. Sci. Technol. 1 (1970) 287.

[2] S. Patai and Y. Halpern, Israel J. Chem. 8 (1970) 655.

[3] A. Basch and M. Lewin, J. Polym. Sci., Polym. Chem. Ed. 11 (1973) 3071.

[4] T. Yurugi, H. Iwata, M. Michio, Nippon Kagaku Kaishi (1975) 733.

[5] W.E. Franklin, J. Macromol. Sci., Chem. A19 (1983) 619.

[6] D.P. Koullas, E. Lois, E.G. Koukios, Biomass Bioenergy 1 (1991) 199.

[7] O.P. Golova, A.M. Pakhomov, E.A. Andrievskaya, R.G. Krylova, Dokl. Akad. Nauk, SSSR 115 (1957) 1122.

[8] A. Basch, M. Lewin, J. Polym. Sci., Polym. Chem. Ed. 11 (1973) 3095.

[9] Y. Halpern, S. Patai, Israel J. Chem. 7 (1969) 673.

[10] O.P. Golova, R.G. Krylova, Dokl. Akad. Nauk, SSSR 116 (1957) 419.

[11] A. Broido, A.C. Javier-Son, A.C. Ouano, E.M. Barrall, J. Appl. Polym. Sci. 17 (1973) 3627.

[12] A. Paucault, G. Sauret, Compt. Rend. Acad. Sci. 246 (1958) 608.

[13] D.-Y. Kim, Y. Nishiyama, M. Wada, S. Kuga, T. Okano, Holzforschung 55 (2001) 521.

[14] H. Kawamoto, W. Hatanaka, S. Saka, J. Anal. Appl. Pyrolysis 70 (2003) 303.

[15] L. Segal, J.J. Creely, A.E. Martin, Jr., C.M. Conrad, Textile Res. J. 29 (1959) 786.

[16] L.E. Alexander, X-Ray Diffraction Methods in Polymer Science, Robert E. Krieger Publishing Co., New York, 1979, p.423.

[17] H. Kawamoto, M. Murayama, S. Saka, J. Wood Sci. 49 (2003) 469.

[18] A.A. Robertson, Tappi 53 (1970) 1331.

[19] S.S. Arslanov, Uzbekskii Khimicheskii Zhurnal (1994) 42.

[20] M.M. De Souza Lima, R. Borsali Macromol. Rapid Commun. 25 (2004) 771.

[21] F.A. Carey, R.J. Sundberg, Advanced Organic Chemistry Part A: Structure and Mechanism, Plenum Press, New York, 1990, p232.

[22] M.J. Antal Jr, Adv. Solar Energy 2 (1985) 175.

Legends of Figures

Fig. 1 X-ray diffraction profiles of the residues obtained from the cellulose pyrolysis in sulfolane at 330 °C.

Fig. 2 Change in the amount of the residual cellulose, crystallinity and relative crystallite size during cellulose pyrolysis in sulfolane at 200, 240 and 330 °C.

a: 330 °C, **b**: 240 °C, **c**: 200 °C,

○: residual cellulose, ●: relative crystallite size, ▲: crystallinity.

Fig. 3 Relationships of crystallinity and relative crystallite size with the recovered yield of cellulose during cellulose pyrolysis in sulfolane at 200, 240 and 330 °C.

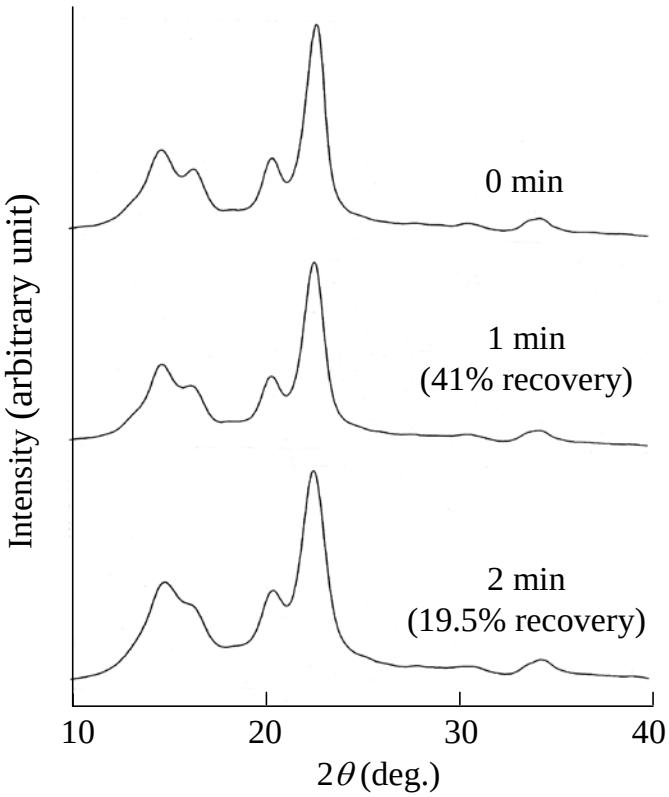
a: crystallinity, **b**: relative crystallite size, ○: 330 °C, △: 240 °C, □: 200 °C.

Fig. 4 Change in the crystallinity and relative crystallite size during pyrolysis of cellulose in nitrogen and dioctyl phthalate at 330 °C.

a: crystallinity, **b**: relative crystallite size, ○: in nitrogen, △: in dioctyl

phthalate.

Fig. 5 A heterogeneous mechanism indicated for the cellulose pyrolysis in sulfolane.



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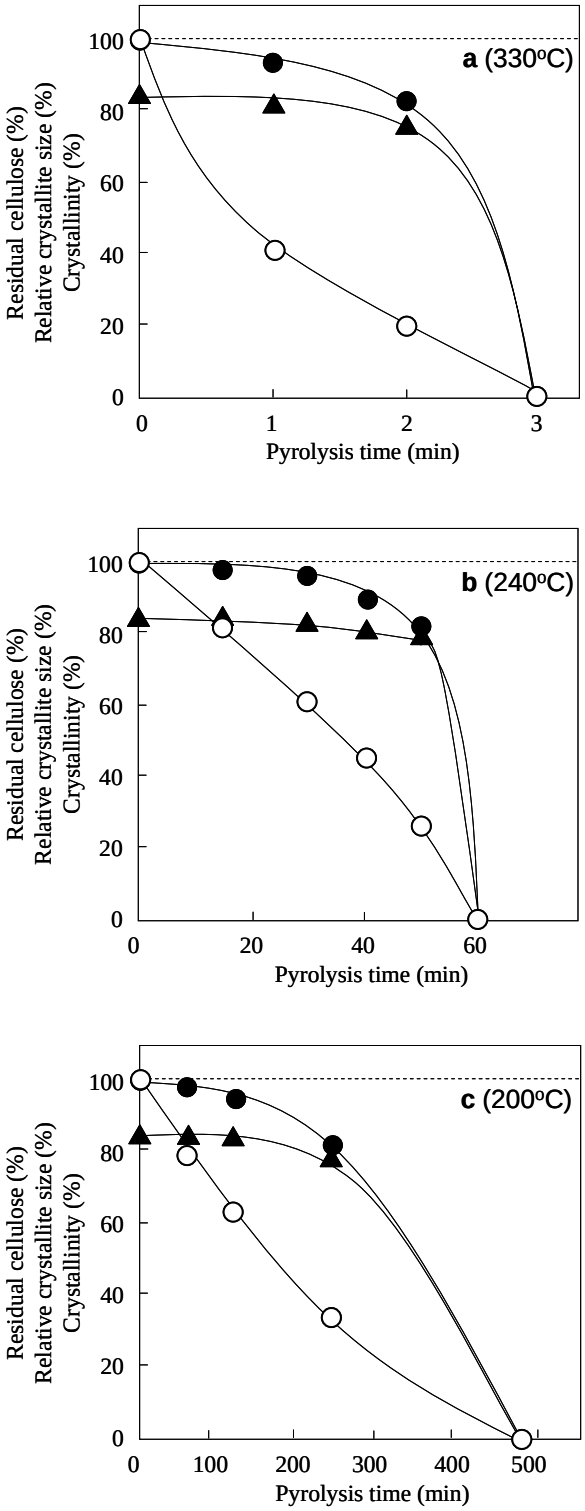

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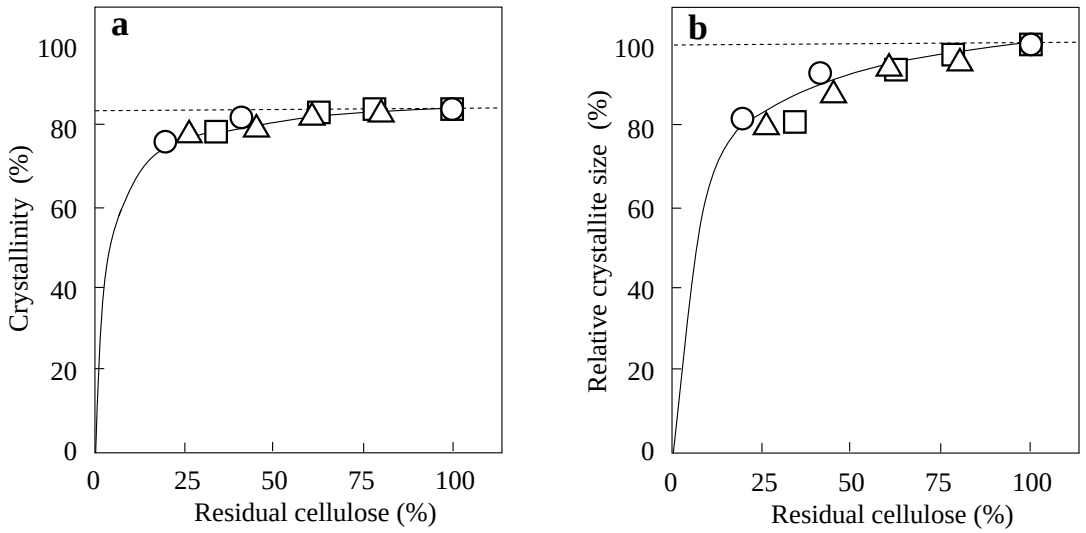

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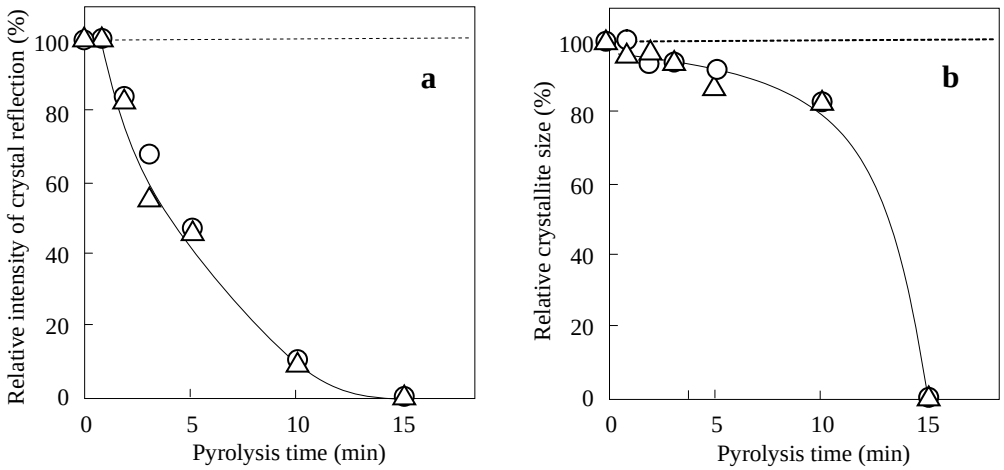

Fig. 4 Change in the crystallinity and relative crystallite size during pyrolysis of cellulose in nitrogen and dioctyl phthalate at 330 °C.
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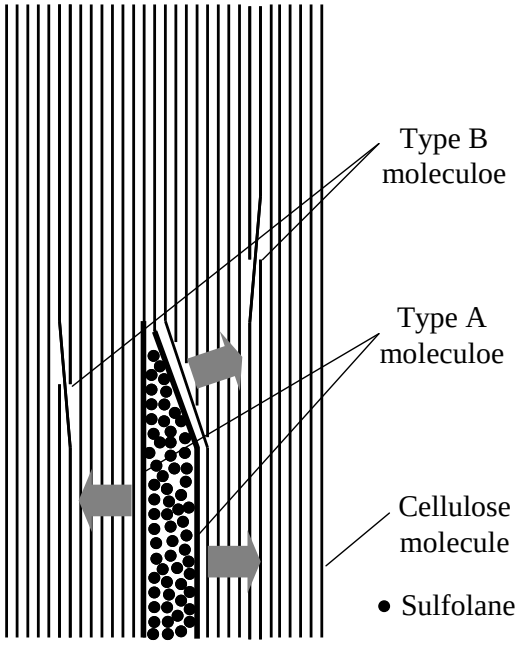

Fig. 5 A heterogeneous mechanism indicated for the cellulose pyrolysis in sulfolane.